# Measurement of NO₂ by Photolysis Conversion Technique

# During TRACE-P

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**Abstract**

An airborne instrument for *in-situ* measurements of tropospheric nitrogen dioxide ($NO_2$) was developed using a photolytic conversion technique followed by chemiluminescence detection of NO.   This instrument was used for the measurements of $NO_2$ onboard the NASA P-3B aircraft during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign. Comparison in the laboratory indicated less than 10 % difference between our $NO_2$ instrument and two independent laser-induced fluorescence instruments.   The magnitudes of potential errors in airborne tropospheric $NO_2$ measurements were further assessed using TRACE-P data set.   The systematic errors estimated for the median $NO_2$ mixing ratios were 19 % (39 %) at 0 - 2 km (2-8 km).   The random errors for a 10 s integration time were estimated to be 5-10 % depending on altitudes.   The observed $NO_2$ mixing ratios were compared with those calculated by a photochemical box model.   Overall, the calculated $NO_2$ values correlated well with those observed ($r^2 = 0.97$), although the calculations were systematically higher than the observations by about 30 %.

**1. Introduction**

Nitrogen oxides ($NO_x = NO + NO_2$) play a critical role in tropospheric photochemistry, especially acting as a catalyst for the formation of ozone ($O_3$).   The major sources of $NO_x$ in the global troposphere are fossil fuel combustion and biomass burning, while aircraft emissions and lightning are also important sources in the upper troposphere [e.g., *WMO*, 1998].   $NO_x$ is mostly emitted in the form of NO and the oxidation of NO into $NO_2$ occurs via the following reactions with ozone and peroxy radicals:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad\qquad (R1)$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad\qquad (R2)$$

$$NO + RO_2 \rightarrow NO_2 + RO \qquad\qquad (R3)$$

where R denotes the alkyl radical.    The photolysis of $NO_2$ followed by reaction with $O_2$ produces $O_3$.

$$NO_2 + h\nu \rightarrow NO + O \qquad\qquad (R4)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad\qquad (R5)$$

Reactions (R1) - (R4) rapidly lead to photochemical equilibrium between NO and $NO_2$ on a time scale of minutes.    Thus, the ambient $NO_2$ mixing ratios can be calculated from equation (1):

$$[NO_2] = \frac{[NO](k_1[O_3] + k_2[HO_2] + k_3[RO_2])}{J[NO_2]} \qquad\qquad (1)$$

where $k_1$, $k_2$, $k_3$, and $J(NO_2)$ are the rate coefficients of the reactions (R1), (R2), (R3), and (R4), respectively.    Observations of NO, $O_3$, and $J(NO_2)$, are often readily available.    The values of peroxy radicals, i.e., $HO_2$ and $RO_2$, can be obtained from either photochemical model calculations or *in-situ* observations.    However, the measurements of these peroxy radical are proven to be much more difficult than that of $NO_2$.    Up to now, the peroxy radical measurement technique has been considered to be in a developing stage.    Many studies in the late 1970s and early 1980s have used observed $NO_2$ to NO ratio to test for the presence of the peroxy radicals, which was recognized as a critical factor in the assessment of ozone photochemical production.    Later studies have even attempted to use this ratio to estimate

the level of the peroxy radicals under rural and remote environmental conditions [e.g., *Ridley et al.*, 1992; *Thornton et al.*, 2002]. Even to this date, measurement of $NO_2$ can still provide a quite valuable test point for models, considering the large uncertainties involved in NMHC oxidation mechanisms and the difficulties in direct measurement of the peroxy radicals. In addition, the $NO_2$ measurement can be considered as critical in determining $NO_x$ levels for nighttime and highly spatial inhomogeneous conditions.

Various attempts have been made for *in-situ* $NO_2$ measurements. There have been a few documented direct LIF measurements [e.g., *George and O'Brien*, 1991; *Thornton et al.*, 2000; *Matsumi et al.*, 2001; *Matsumoto et al.*, 2001]. This type of the system, however, has not been widely used in field studies. The reported limit of detection (LOD) ranged from 15 to 450 parts per trillion by volume (pptv). A more conventional approach involves photolytic conversion of $NO_2$ to NO followed by a measurement of NO. The concurrent measurement of ambient NO allows for determination of ambient $NO_2$ by subtraction. For example, a photofragment/two-photon laser-induced fluorescence (PF/TP-LIF) system developed by Georgia Institute of Technology (GIT) researchers has been used to measure ambient $NO_2$ in NASA Global Tropospheric Experiment (GTE) airborne field missions for over a decade [e.g., *Bradshaw et al.*, 1999]. The reported LOD is typically 2 pptv for a 3 min integration time.

The $NO-O_3$ chemiluminescence detector (CLD) combined with an $NO_2$ photolysis system has been the most widely used for *in-situ* $NO_2$ observations. This type of system can be characterized as fast-response, high-precision, and relatively simple [e.g., *Kley and McFarland*, 1980; *Ridley et al.*, 1988; *Gao et al.*, 1994; *Ryerson et al.*, 2000]. In this type of system, the $NO_2$ molecules in the sample air are converted to NO in a photolysis cell by ultraviolet (UV) light and sent to an NO CLD. We have developed an airborne instrument for the measurements of $NO_2$ using this technique. The basic configuration of the instrument is the same as that described by *Gao et al.* [1994]. However, their instrument

was originally designed for stratospheric measurements and it has not been fully tested for tropospheric conditions.   In this paper, we describe the performance of the chemiluminescence/photolysis $NO_2$ instrument on the NASA P-3B aircraft during the Transport and Chemical Evolution over the Pacific (TRACE-P) mission, which was conducted between February and April, 2001 [*Jacob et al.,* this issue].   Also reported here are the results from the comparison of the observed $NO_2$ mixing ratios with those calculated by a photochemical box model.


## 2. Instrumentation

The configuration of our $NO_2$ instrument is basically the same as that developed by *Gao et al*. [1994] and *Del Negro et al*. [1999], and only important points are given here.   Figure 1 shows a schematic diagram of the photolytic conversion system.   It consists of a photolysis cell, metal halide lamp, optical filters, shutter, and cooling fans.   Important parameters of this system are summarized in Table 1.   Ambient $NO_2$ is partially converted to NO and then detected by an $NO-O_3$ CLD described in *Kondo et al*. [1997].   The whole $NO_2$ measurement system consists of an NO detector (NO channel) and an independent NO detector combined with the photolytic conversion system ($NO_2$ channel).   Both long pass (UTF-50S-34U, Hoya Inc., Tokyo, Japan) and band-pass (BLF-50S-380B, Hoya Inc.) filters were mounted in front of the photolysis cell.   As shown in Figure 2, the Borosilicate glass (Pyrex[®]) window of the cell, together with these filters prevented UV radiation shorter than 320 nm from entering the cell.   Borosilicate glass also absorbs some of the IR radiation ( $\lambda$ > 2700 nm) and the BLF-50S-380B blocks visible and near IR radiation [*Gao et al*., 1994].   Since the $HNO_3$ absorption cross section increases rapidly with decreasing wavelength shorter than about 340 nm, the long-pass filter is important to prevent the photolysis of $HNO_3$.

The residence time of sample air in the photolysis cell is about 1.1 s at a sample flow rate

of 2.25 standard liters per minute (slm) and a cell pressure of 80 hPa.   The effect of the

thermal decomposition of PAN, $HO_2NO_2$, and $N_2O_5$ on the $NO_2$ measurements for these

conditions was calculated in same way as was done in *Gao et al.* [1994].   The fractions of

these molecules dissociated in the cell are shown in Figure 3 as a function of the cell

temperature.   The cell temperature was controlled at 15°-25°C by the cooling fans during

TRACE-P.   The contributions from thermal decomposition of these species to the $NO_2$

measurements during TRACE-P are summarized in Table 2.   These effects are negligibly

small for the measurements below 8 km, which was the maximum altitude of the P-3B.


**3. Data Processing and Error Analysis**

   Mixing ratios of $NO_2$ ([$NO_2$]) were derived from the following formula using the measured

parameters.


$$[NO_2] = \frac{C_{total} - (BG + A_{NO2}) - S_{NO}[NO]F}{S_{NO2}} \qquad (2)$$


where $C_{total}$ represents the photon count signal of the $NO_2$ channel (Hz), BG is the background

signal (Hz), $A_{NO2}$ is the artifact signal (Hz) caused by the illumination of the photolysis cell

by the UV light, $S_{NO2}$ ($S_{NO}$) is the sensitivity of the $NO_2$ (NO) channel in Hz/pptv, and [NO] is

the NO mixing ratio (pptv) measured by the NO channel.   F is the NO counts correction

factor, defined as the ratio of the NO mixing ratios measured by the NO and $NO_2$ channels

[*Gao et al., 1994*].   The conversion efficiency (not explicitly shown in equation (2)) is

defined as the ratio of photolyzed $NO_2$ to ambient $NO_2$.   $S_{NO}$, $S_{NO2}$, and the conversion

efficiency were measured by adding standard calibration NO and $NO_2$ gases into the sample

air and $A_{NO2}$ were measured by sampling zero air.   The values of $S_{NO}$, $S_{NO2}$, conversion

efficiency, F, and $A_{NO2}$ were measured about 10 times and BG was measured about 50 times

per 8-hour flight during TRACE-P.   Typical values of these parameters, together with the variabilities (1-sigma) of $A_{NO2}$ and BG during TRACE-P are given in Table 1.

Contribution of the ambient NO to the signals of the $NO_2$ channel was estimated by the term $S_{NO}[NO]F$.   The BG signals are caused by dark counts of the photomultiplier tube (PMT), noise from cosmic rays, and photo-emission due to the reaction of the ozone with walls of the reaction vessel of the CLD.   $A_{NO2}$ is considered to be caused by the release of NO or $NO_2$ from the wall of the cell by reactions involving other ambient reactive nitrogen species under UV illumination [*McFarland et al.*, 1986; *Gao et al.*, 1994].

The median profiles of NO, $NO_2$, and the $NO/NO_2$ ratio during TRACE-P are shown in Figure 4.   The median $NO_2$ values were higher than 50 pptv below 2 km and decreased with altitude.   By contrast, the NO mixing ratios were nearly constant independent of altitude, resulting in an increase in the $NO/NO_2$ ratio with altitude.

### 3.1. Systematic Errors

The total systematic error can best be estimated using the uncertainties in each component in equation (2).   The uncertainty in $S_{NO2}$ was defined as the sum of the accuracy and the precision in the $NO_2$ sensitivity.   The accuracy of $S_{NO2}$ was determined from the accuracies in the estimate of the mass flows of sample air and calibration $NO/N_2$ gas and the NO and $NO_2$ concentrations of the calibration gas [*Gao et al.,* 1994].   The precision of $S_{NO2}$ was determined from fluctuations in the sensitivities obtained by each calibration.   The $S_{NO2}$ value was quite stable during the observations at all altitudes.   During TRACE-P, we estimated the accuracy of $S_{NO2}$ to be 9 %.   Uncertainties in BG and $A_{NO2}$ were estimated from their measured variabilities during the flights.   After considering the systematic uncertainty for each term, the systematic error for the $NO_2$ measurements can be expressed as follows:

$$\frac{\Delta[NO_2]}{[NO_2]} = \left\{ \left(\frac{\Delta S_{NO2}}{S_{NO2}}\right)^2 + \left(\frac{\Delta BG}{S_{NO2}[NO_2]}\right)^2 + \left(\frac{\Delta A_{NO2}}{S_{NO2}[NO_2]}\right)^2 + \left(\frac{S_{NO}[NO]F}{S_{NO2}[NO_2]} \cdot \frac{\Delta F}{F}\right)^2 \right\}^{\frac{1}{2}} \qquad (3)$$

Among the terms in equation (3), we have found that $A_{NO2}$ typically has the largest contribution and the calibration factor $S_{NO2}$ and background are the other two important factors.   In addition, the accuracy of the $NO_2$ measurement has a dependence on the partitioning of $NO_x$, i.e., $[NO]/[NO_2]$ ratio.   The last term in equation (3) becomes significant at high altitudes where $[NO]/[NO_2]$ becomes larger than unity.   As examples, the systematic errors are summarized in Table 3.   We estimated the systematic errors for our $NO_2$ instrument to be 19 and 39 % for the altitudes below and above 2 km, respectively.

## 3.2. Random Errors

Assuming that the observed 1-s photon counts follow a Poisson distribution, the signal-to-noise (S/N) ratio for the integration time of 1 s can be calculated as follows:

$$S/N = \frac{C_{meas}}{\sqrt{C_{total} + C_{SUB}}} = \sqrt{S_{NO_2}} \times \frac{[NO_2]}{\sqrt{[NO_2] + 2[NO_2]_{SUB}}} \qquad (4)$$

where

$C_{SUB}$: photon count rate to be subtracted from total count rate (i.e., total of BG, $A_{NO2}$, and ambient NO)

$C_{meas}$: net photon count rate due to ambient $NO_2$ ( $= C_{total} - C_{SUB}$)

$[NO_2]_{SUB}$: $C_{SUB}$ signal expressed in $NO_2$ equivalent ( $= C_{SUB}/S_{NO2}$)

Using equation (4), the random error (1-sigma) for the integration time of t (s) can be calculated as follows:

$$\text{Random Error}(1\sigma) = \frac{[NO_2]}{(S/N)} = \frac{\sqrt{[NO_2] + 2[NO_2]_{SUB}}}{\sqrt{S_{NO_2}}} \times \frac{1}{\sqrt{t}} \qquad (5)$$

$$\text{Nominal } LOD(2\sigma) = \frac{\sqrt{2[NO_2]_{SUB}}}{\sqrt{S_{NO_2}}} \times \frac{2}{\sqrt{t}} \qquad (6)$$

The random error in the 10 s averaged $NO_2$ measurements during TRACE-P is also summarized in Table 3.   True LOD (13 pptv) is a sum of nominal LOD (4 pptv) and fluctuation of $A_{NO2}/S_{NO2}$ (9 pptv).   It should be noted that these values were close to the natural fluctuations in the $NO_2$ values measured in comparatively uniform air masses.   For example, $NO_2$ mixing ratios were stable at 65 pptv at 1.3 km during 5760-6010 s and 32 pptv at 3 km during 6660-6940 s on March 23, 2001.   The natural fluctuations of the $NO_2$ values during these periods were 7 % and 13 %, which are close to the estimated precision.

## 4.   Intercomparisons with LIF Instruments

The CLD instrument was compared in the laboratory with two independent laser-induced fluorescence (LIF) instruments which are capable of making direct $NO_2$ measurements.   The first comparison was made against the LIF instrument (LIF-1) developed by *Matsumi et al.* [2001], where details of the results of the comparison are also given.   In the LIF-1 measurements, the laser wavelength was fixed at the top and bottom absorption positions around 440 nm.   The sensitivity was estimated to be 30 pptv in 10 s and S/N = 2.   The standard $NO_2$ calibration gas produced by oxidation of NO by $O_3$ was sampled simultaneously by the CLD system and LIF-1 instrument.   In addition, the air outside of the

laboratory of the Solar-Terrestrial Environment Laboratory, Nagoya University in Toyokawa,

Japan was also sampled after diluted with zero air by a factor of up to 200.    This diluted air

was sampled simultaneously by the CLD and LIF-1 instruments.    As shown by *Matsumi et*

*al.* [2001], the result of the overall comparison is expressed as

$$[NO_2]_{LIF-1} = (1.09 \pm 0.05) \, [NO_2]_{CLD} + (9.0 \pm 11.6)$$

$$([NO_2]_{LIF-1} = 30\text{-}900 \text{ pptv}; \, r^2 = 0.99) \qquad (7)$$

where $[NO_2]_{LIF-1}$ and $[NO_2]_{CLD}$ are the $NO_2$ mixing ratios in pptv measured by the LIF-1 and

CLD instruments.    The accuracy of the LIF-1 measurement is estimated to be 15 %.    The

agreement was even better when only the data below 400 pptv were used.    *Matsumi et al.*

suggested that the systematic difference between the two systems is most likely less than

10 %, which is well within the reported systematic uncertainty for each of these systems.

   The second comparison was made with the different type of the LIF instrument (LIF-2)

described in *Matsumoto et al*. [2001].    The simultaneous measurements were made by

directly sampling polluted air outside of our laboratory in Tokyo.    The results of the

comparison are shown in Figure 5 and the relationship between the two measurements is

given as

$$[NO_2]_{LIF-2} = (1.012 \pm 0.004) \, [NO_2]_{CLD} - (894 \pm 101) \quad (r^2 = 0.99) \qquad (8)$$

where the $NO_2$ mixing ratios are expressed in pptv.    The LOD of the LIF-2 used for the

second intercomparison is 4 pptv for a 1 min integration time (Matsumoto et al., unpublished

data).    The $NO_2$ mixing ratios ranged from 10 to 50 parts per billion by volume (ppbv)

during the intercomparison.    These intercomparisons demonstrate that our $NO_2$

measurements agreed with the LIF measurements on the ground to within 10 %, which is within the combined accuracy of each measurement, in the $NO_2$ range of 30 pptv to 50 ppbv.

## 5. Comparison with Model Calculations

For comparison with the observed $NO_2$ values, the photostationary state $NO_2$ mixing ratios were calculated by a photochemical box model [*Davis et al.*, 1996; *Crawford et al.*, 1996; 1997] using the simultaneously observed NO, $O_3$, and $J(NO_2)$ values.    In this calculation, the model calculated peroxy radical levels were further scaled to match the sum of $HO_2$ and $RO_2$ observed by *Cantrell et al.* [this issue].    Assuming that the model predicted partitioning of calculated $HO_2$ and $RO_2$ is consistent with that of the observations, the photostationary state $NO_2$ based on observed $HO_2 + RO_2$ can be calculated using equation (9).

$$[NO_2]_{calc} = \frac{k_1[O_3][NO]}{J(NO_2)} + \left( k_2[HO_2] + \sum_i k_i[R_iO_2] \right)_{calc} \frac{\left( HO_2 + \sum_i R_iO_2 \right)_{obs}}{\left( HO_2 + \sum_i R_iO_2 \right)_{calc}} \cdot \frac{[NO]}{J(NO_2)} \quad (9)$$

It should be noted here the difference between the model $NO_2$ cited in *Olson et al.* [this issue] and $[NO_2]_{calc}$ here is that *Olson et al.* calculated $NO_2$ levels using model predicted peroxy radical levels without further scaling by the observations.    However, the resulting $NO_2$ levels from both approaches are quite similar.    For over 3700 individual points having both model and observed peroxy radicals, the median $NO_2$ ratio between these two calculations was estimated to be 1.01, with *Olson et al.* being slightly higher.    The 5th and 95th percentile values are 0.78 and 1.24, respectively.    Furthermore, these two sets of data are highly correlated with an $r^2$ value of 0.99.    The reason for this close agreement reflects the fact that ambient $NO_2$ is predominantly controlled by the reactions (R1) and (R4) and all

critical parameters involved in these processes were constrained to observed values in both models.   Therefore, the result from this analysis is highly consistent with those derived from the analysis by *Olson et al.*

In equation (9), the $O_3$ mixing ratios used here were measured with the $NO$-$O_3$ chemiluminescence technique and $J(NO_2)$ was measured with a scanning actinic flux spectroradiometer (SAFS) [*Shetter et al.*, 2002; *Lefer et al.*, this issue].   Comparisons of the observed and calculated $NO_2$ were made only for the periods when $[HO_2 + RO_2]$ were observed simultaneously.   As a result, about 2300 60 s data points can be used for the comparison.   The observed values of $O_3$, $HO_2 + RO_2$, and $J(NO_2)$ used in model calculations are shown in Figure 6 as a function of altitude.

Uncertainties in the calculated $NO_2$ values are caused by the uncertainties in the parameters on the right hand side of equation (1).   These uncertainties are listed in Table 4. Uncertainties in the rate constants were estimated at 273 K [*Sander et al.*, 2003].   The overall systematic uncertainty in calculated $NO_2$ was estimated from error propagation analysis to be 27 %.   This overall uncertainty can be mostly attributed to the systematic uncertainties associated with the reaction (R1) and (R4), resulting from the fact, again, that these two reactions are typically the dominant processes controlling the cycling between $NO$ and $NO_2$.

As discussed earlier, the $NO_2$ values calculated for each 60-s interval by the box model are used for comparison.   A data filter was applied to select the points that were sampled in nearly cloud free conditions, i.e., $0.8 \leq JIF \leq 1.2$.   JIF is *J*-value impact factor defined as the $J(NO_2)$ ratio of observation to clear sky model [*Lefer et al.*, this issue].   This filter is to minimize the potential effect of clouds and aerosols, which may perturb ambient $NO_2$ and $NO$ photochemical equilibrium.   The range of observed $NO_2$ selected for this comparison is 13 to 1000 pptv.   The lower limit is 2 times of $NO_2$ instrument LOD, i.e., 13 pptv.   The upper

limit reflects that almost all the observed $NO_2$ values during TRACE-P were typically lower than 1000 pptv except for take off and landing. In addition, the data points were removed if their NO values were lower than 2 pptv, i.e., 2 times the NO instrument LOD. The final data set contained nearly 1015 data points.

Figure 7 shows an example time series of 10 s averages of NO and $NO_2$ measurements and model calculated $NO_2$ over the Pacific Ocean south of Japan on March 23, 2001. The observed spatial changes in $NO_2$ well follow the NO changes within 10 seconds. The calculated $NO_2$ values also follow the observed changes, although the model values are somewhat higher.

Figure 8 displays the correlation between model calculated $NO_2$, $[NO_2]_{calc}$, and 60 s averaged $NO_2$ observations, $[NO_2]_{obs}$. The $r^2$ value calculated for this 60 s data set was 0.97 and the median ratio of model to observation, i.e., $[NO_2]_{calc}/[NO_2]_{obs}$ (M/O), was 1.2 with the upper and lower quartiles being 0.9 and 1.4, respectively. The dependence of this ratio on the observed $NO_2$ level is modest. Generally the data with $NO_2$ values lower than 60 pptv (~containing 75 % data) tend to have somewhat smaller M/O ratios. A more detailed analysis, however, revealed a significant altitude trend in M/O ratio as shown in Figure 9. For altitude range of 0-4 km, the M/O ratio remained nearly constant having values close to 1.3. This ratio decreases with altitude, with the lowest values found between 6 and 7 km. There are about 170 data points in this altitude range and the median M/O ratio is 0.7, suggesting 30 % model underestimation. Similar trends were seen in the past [*Davis et al.*, 1993; *Crawford et al.*, 1996]. These trends were attributed to suspected instrumental interference. Due to the cold temperature at this altitude, increased amounts of thermally labile $NO_y$ species have always been a concern for potential interference with $NO_2$ measurements [*Bradshaw et al.*, 1999]. Results in Table 4, however, clearly eliminate the prime candidates (e.g., PAN, $HO_2NO_2$, and $N_2O_5$) for such an interference. Despite the

concerns raised by the altitude trend, it also should be noted that this difference is still well within the combined uncertainties from model and observation.

It has been shown earlier that the median difference between model and observations is 30 %, model values being higher.    This difference is quite modest when considering the observational systematic error ranges from 19 to 39 % and the model system bias varies from 22 to 27 %.    However, the model overestimation persists throughout most of the data population, especially those sampled below 4 km.    It is still worthwhile to explore the possible causes for this systematic difference.    Since model values were higher, it can be hypothesized that the observed peroxy radical levels may be biased too high.    To further investigate this hypothesis, the observed $NO_2$ was compared to the model values derived from the so called "simple theory", namely that the cycling between NO and $NO_2$ is controlled only by the reactions (R1) and (R4).    The results shows that the $NO_2$ observations are, on average, about 10 % higher, which suggest a 10 % average peroxy radical contribution to NO to $NO_2$ conversion.    In contrast, the average of model-estimated peroxy radical contribution is 23 %. It should be noted here that both model and observations suggest that the ambient $NO_2$ is not sensitive to ambient variations of peroxy radicals for the conditions encountered during TRACE-P.    Another test carried out in this analysis involves a data subset containing the data points where model-predicted peroxy radical contributions are less than 10 %.    Thus, for these cases, the NO-$NO_2$ cycling should be predominantly controlled by "simple theory", i.e. reactions (R1) and (R4).    The median M/O ratio for this subset is 1.3.    This is significant because the model $NO_2$ merely depends only on observed values of NO, $O_3$, and $J(NO_2)$.    In this case, the shift in model $NO_2$ values is linked to changes in $k_1$ and/or in one or a combination of the above listed variables.    At the same time, it should also be recognized here that the difference between model and observation is very close to the combined uncertainty in model and measurement.

NO$_2$ measurements during the previous NASA GTE aircraft observations generally showed higher values than those calculated [*Crawford et al.*, 1996], as opposed to the present results. The [NO$_2$]$_{calc}$/[NO$_2$]$_{obs}$ ratios obtained by GIT–LIF [*Sandholm et al.,* 1994] over the western Pacific Ocean during Pacific Exploratory Mission-West A (PEM-W-A) were 0.84 and 0.39 at 0-1 and 1-6 km, respectively.    The ratios measured at 1-6 km during Chemical Instrumentation Test and Evaluation 3 (CITE 3), Atmospheric Boundary Layer Experiments 3B (ABLE 3B), and CITE 2 ranged between 0.58 and 0.77, although they were close to 1 during TRACE A.    The [NO$_2$]$_{calc}$/[NO$_2$]$_{obs}$ ratios smaller than one indicated a possibility of decomposition of reactive nitrogen species other than NO$_2$ in the LIF system.    A large uncertainty in the measurements of the $J$(NO$_2$) values by Eppley radiometers during these campaigns is also a potential cause for the significant deviation of the [NO$_2$]$_{calc}$/[NO$_2$]$_{obs}$ ratios from unity.    The [NO$_2$]$_{calc}$/[NO$_2$]$_{obs}$ ratios was in the range between 0.8 and 1.14 at 0-6 km over the tropical South Pacific during Pacific Exploratory Mission to the Pacific tropics A and B (PEM-Tropics A and B) [*Olson et al.*, 2001; *Bradshaw et al.*, 1999; *Schultz et al.*, 1999]. A better agreement between the model and observed NO$_2$ was attributed to the improvement of the LIF system and better $J$(NO$_2$) measurements with the NCAR scanning actinic flux spectroradiometer [*Bradshaw et al.*, 1999].

## 6. Summary

NO$_2$ measurements based on UV photolysis followed by NO detection by CLD were made on board the P-3B during TRACE-P.    The median NO$_2$ mixing ratios were 70 pptv (30 pptv) at 0-2 km (2-8 km).    The systematic errors estimated for the median NO$_2$ mixing ratios were 19 % (39 %) at 0 - 2 km (2-8 km).    The random errors for a 10 s integration time were estimated to be 5-10 % depending on altitudes.    In the laboratory tests, very tight linear relationships (r$^2$ = 0.99) were obtained from the intercomparison of the CLD with two LIF

instruments with a systematic difference less than 10 % for the $NO_2$ range between 30 pptv and 50 ppbv.

Photostationary state values of the $NO_2$ mixing ratio were calculated using the simultaneous measurements of NO, $O_3$, $HO_2 + RO_2$, and $J(NO_2)$. The correlation between the calculated and observed $NO_2$ values was very high ($r^2 = 0.97$). The calculated $NO_2$ values were systematically higher than those observed by 30 %. A systematic cause of this difference was not identified, although the difference is within the uncertainty of the measurements and model estimates. The present analysis indicates that the overall uncertainty of the $NO_2$ measurements made during TRACE-P is about 30 %.

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**Figure captions**

**Figure 1.**  A schematic diagram of the $NO_2$ photolysis system.

**Figure 2.**  Transmittance of the Pyrex window and two filters (BLF-50S-380B, UTF-50S-34U) mounted in front of the photolysis cell.  Thick curve represents the total transmittance.  Product of photochemical quantum yield ($\Phi$) and absorption cross section ($\sigma$) of $NO_2$ ($\Phi\cdot\sigma$) are also shown [*Sander et al.*, 2003].

**Figure 3.**  Gas-phase thermal dissociation fraction of $N_2O_5$, $HO_2NO_2$, and PAN as a function of temperature for a residence time of 1.1 s and pressure of 80 hPa.

**Figure 4.**  Vertical profiles of (a) NO, (b) $NO_2$, and (c) $NO/NO_2$ ratio.  Small dots represent all the 60 s data during TRACE-P and solid circles represent the median values.  Horizontal bars represent 1-$\sigma$ values.

**Figure 5.**  Scatter plot of $NO_2$ measured by LIF-2 ($[NO_2]_{LIF-2}$) versus $NO_2$ measured by CLD ($[NO_2]_{CLD}$).  Small dots represent all the 10 s data.  The solid line represents the regression line.

**Figure 6.**  Vertical profile of the $O_3$, $HO_2 + RO_2$, and $J(NO_2)$.  Small dots represent all the 60 s data and large circles represent median values for each 1 km step.  Horizontal bars represent the 1-sigma of the ratios.

**Figure 7.**  Time series of the $NO_2$ mixing ratios (red line) measured every 10 seconds on March 23, 2001 during TRACE-P.  NO mixing ratios (blue line), model calculated $NO_2$

mixing ratios (black line), and aircraft cruise altitude (dashed line) are also shown.    The

model $NO_2$ values are given every 60 seconds.


**Figure 8.**    Scatter plot of calculated $NO_2$ ($[NO_2]_{calc}$) versus observed $NO_2$ ($[NO_2]_{obs}$).

Small dots represent all the 60 s data.    The solid and dashed lines represent the regression

and one-to-one lines, respectively.


**Figure 9.**    Same as Figure 8 except for the ratios of calculated $NO_2$ ($[NO_2]_{calc}$) to observed

$NO_2$ ($[NO_2]_{obs}$).    Small dots represent all the 60 s data and large circles represent median

values for each 1 km step.    Horizontal bars represent the 1-sigma values.

**Table 1.** Parameters for $NO_2$ Measurements

| | |
|---|---|
| Cell pressure (hPa) | 80 |
| Cell temperature (°C) | 20 (15-25) |
| Cell volume ($cm^3$) | 500 |
| Cell sample flow (slm) | 2.25 |
| Residence time (s) | 1.1 |
| $S_{NO}$ (Hz/pptv) | 14 |
| $S_{NO2}$ (Hz/pptv) | 7 |
| Conversion efficiency (%) | $50 \pm 3$ |
| F | $1.0 \pm 0.1$ |
| $BG/S_{NO2}$ (pptv) | $100 \pm 5$ |
| $A_{NO2}/S_{NO2}$ (pptv) | $25 \pm 9$ |

**Table 2.** Effect of Thermal Decomposition on $NO_2$ Mixing Ratio

| Species | Mixing Ratio pptv; 6-8 km | Fraction Dissociated % | Effect on $NO_2$ [a] % |
|---|---|---|---|
| PAN | 72 [b] | 0.021 | 0.08 |
| $HO_2NO_2$ | 13 [c] | 1.0 | 0.70 |
| $N_2O_5$ | 0.1 [c] | 1.6 | 0.01 |

a) For the median $NO_2$ mixing ratio of 19 pptv at 6-8 km during TRACE-P.
b) Median value at 6-8 km during TRACE-P.
c) Median value at 6-8 km calculated by the box model for TRACE-P.

**Table 3.** Systematic and Random Errors in the $NO_2$ Mixing Ratio

| Error | | $NO_2$ = 70 pptv (< 2 km) % | $NO_2$ = 30 pptv (> 2 km) % |
|---|---|---|---|
| Systematic | $S_{NO2}$ | 9 | 9 |
| | BG | 7 | 16 |
| | $A_{NO2}$ | 13 | 30 |
| | $NO_{SUB}$ | 9 | 16 |
| | Total | 19 | 39 |
| Random | 10 s ave. | 5 | 10 |

**Table 4.** Uncertainties in the $NO_2$ Model Calculation

| Parameters | Accuracy (%) |
| --- | --- |
| $[O_3]$ | 5 |
| $[HO_2 + RO_2]$ | 35 |
| $[NO]$ | 10 |
| $J(NO_2)$ | 8 |
| $k_1$ (273 K) | 17 |
| $k_2$ (273 K) | 17 |
| Total error | 27 |